Fontana, WI

SOLID OXIDE MEMBRANE PROCESS FOR THE REDUCTION OF OXIDES IN SPENT NUCLEAR FUEL

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Outline

- Overview of the SOM Process
  - SOM Process for Magnesium Production
  - SOM Process with Electrolytic Refining for Recycling Magnesium Alloys
  - SOM Process for Silicon Production
- SOM process for Uranium oxide reduction in spent nuclear fuel
  - Identify surrogate for Uranium oxide
  - Identify fluoride flux for dissolving the surrogate oxide
  - Determine stability of YSZ membrane in the chosen flux
  - Determine stability of reduced metal and flux-surrogate oxide system with cathode and crucible material
  - Perform and Characterize SOM electrolysis employing the flux with the surrogate oxide
  - Characterize Deposit and YSZ membrane
- Conclusions and Future Work

Schematic of the SOM Process for the Production of Metals

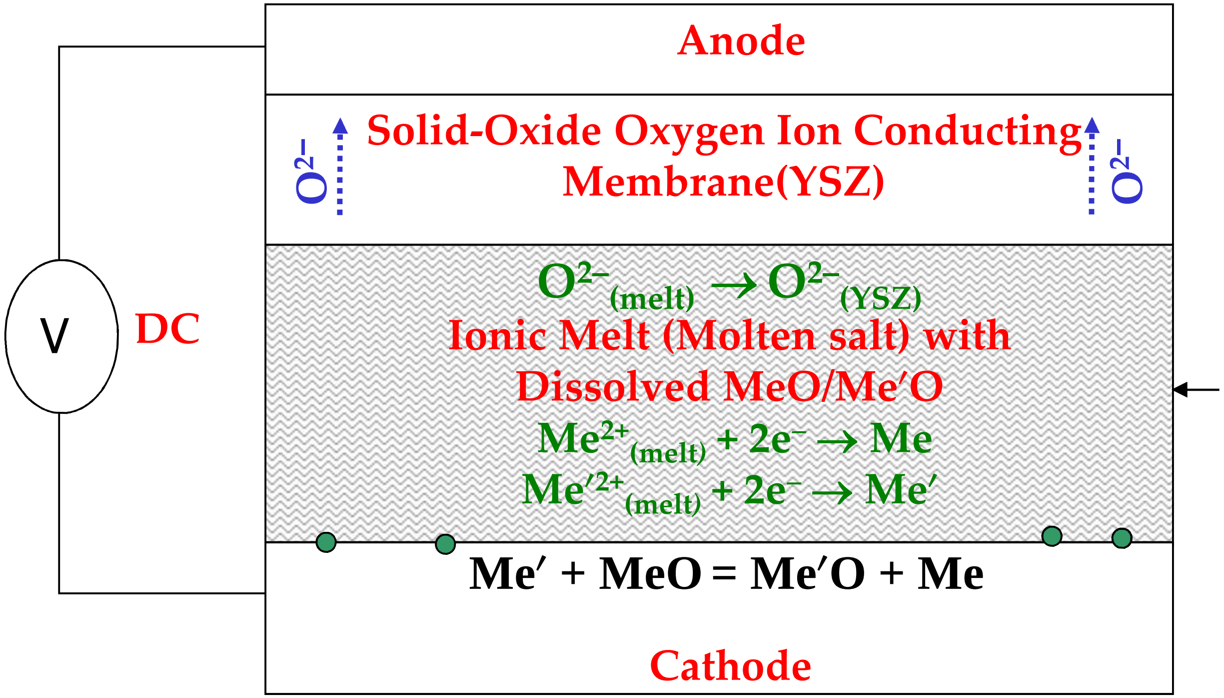
$$CH_4(g) + O^{2-}_{(YSZ)} \rightarrow CO(g) + 2H_2(g) + 2e^-$$

$$H_2(g) + O^{2-}_{(YSZ)} \rightarrow H_2O(g) + 2e^-$$

$$C + O^{2-} \rightarrow CO(g) + 2e$$

$$CO(g) + O^{2-}_{YSZ} \rightarrow CO_2(g) + 2e^-$$

$$O^{2-} \rightarrow \tfrac{1}{2} O_2(g) + 2e$$



- No electronic conductivity
- High Ionic Conductivity
- Oxide solubility
- Low viscosity
- Low volatility
- Stable

SOM Process (Mg, Si, Yb, Ca, Ta, and Ti)

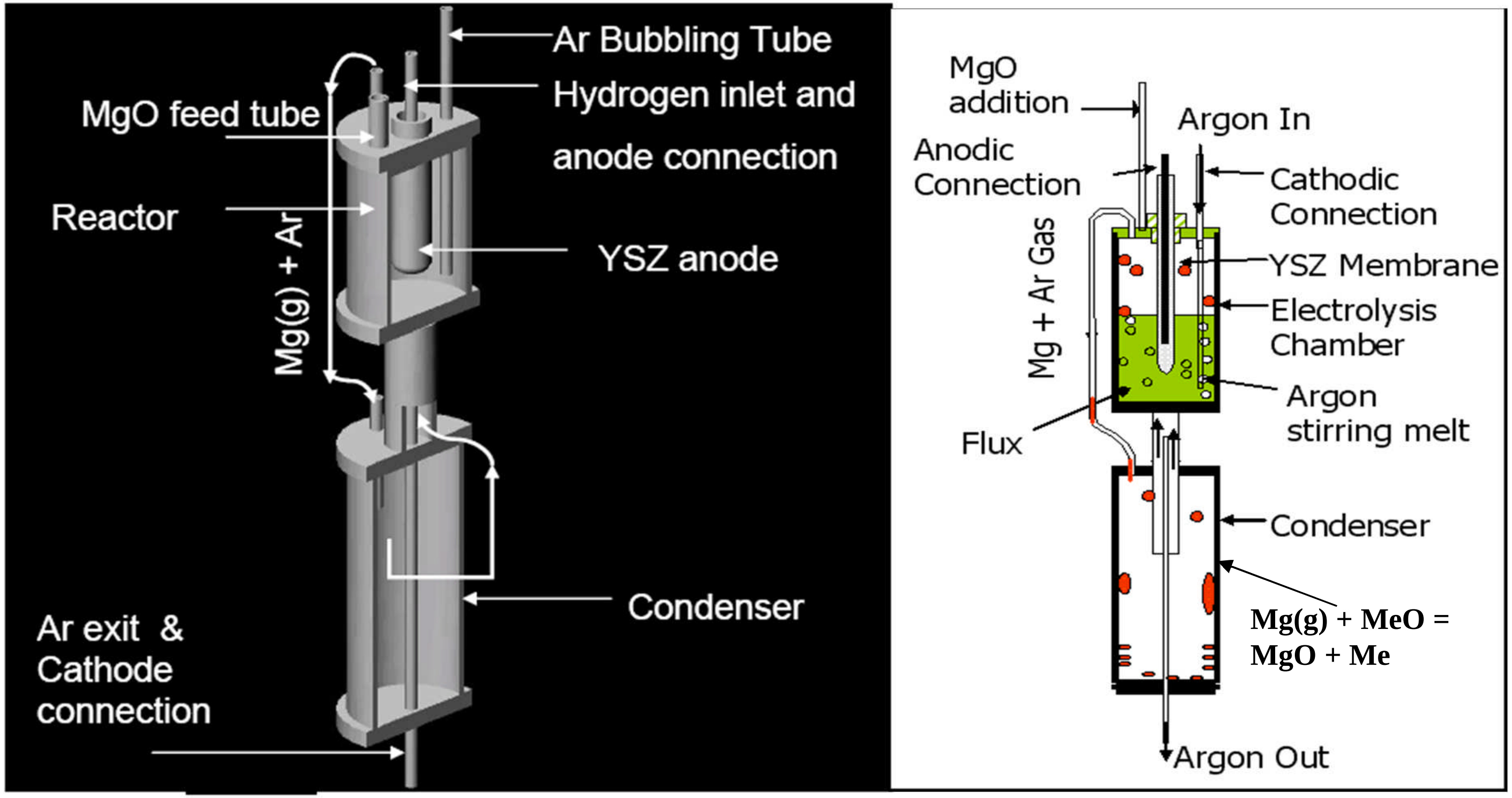
State-of-the-art Electrolysis

- Halide feed preparation
- Higher dissociation potential
- Higher energy requirement
- Environmentally Hazardous
  - Chlorine and its byproducts form at the anode
- Higher capital Cost

SOM Electrolysis

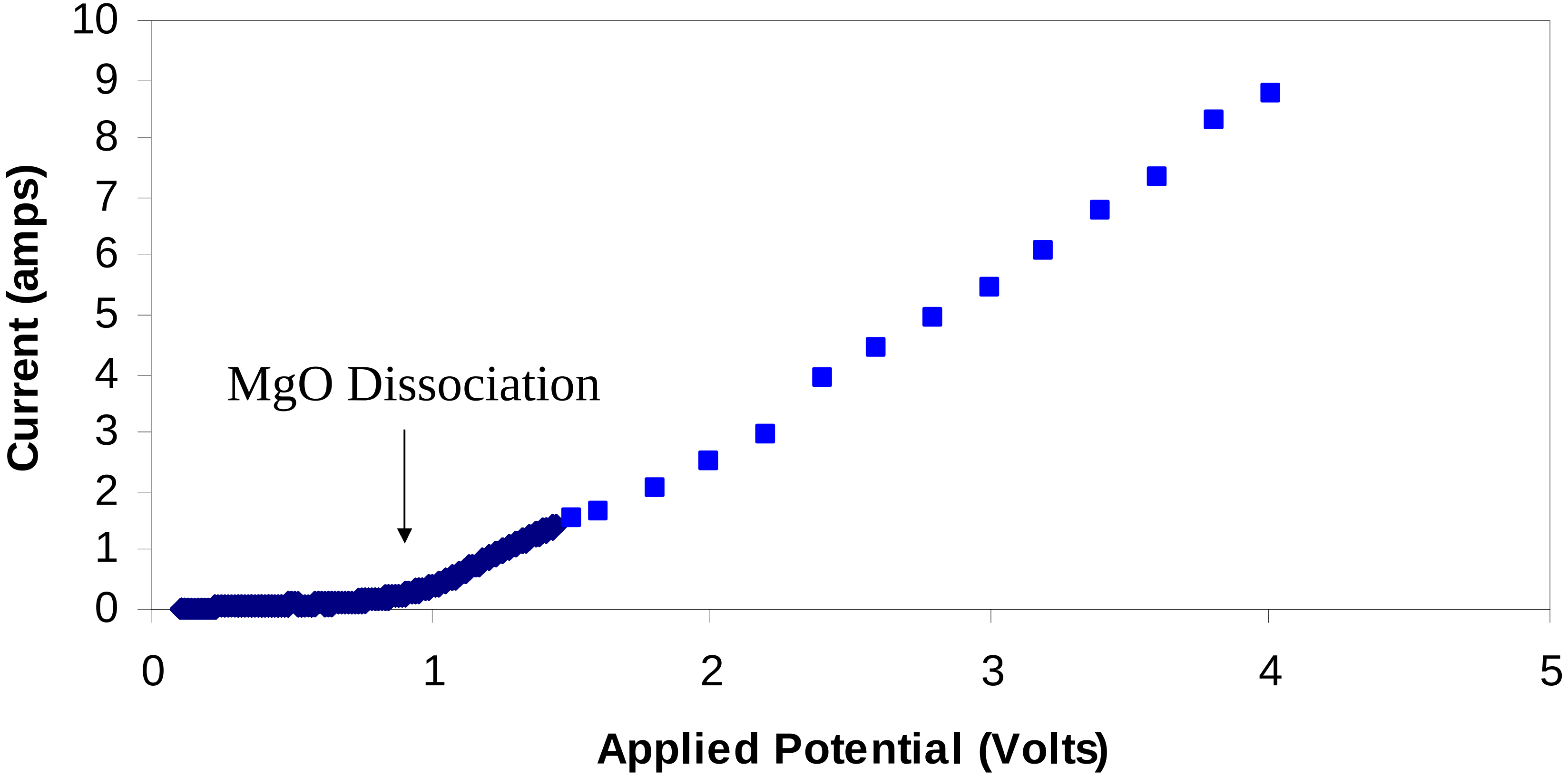
- Little or no oxide feed preparation
- Lower dissociation potential
- Lower energy requirement
- Environmentally friendly
  - Oxygen evolution at the anode
- Lower capital cost

Experimental Single Tube SOM Reactor for Magnesium Production(100-200 g/day)



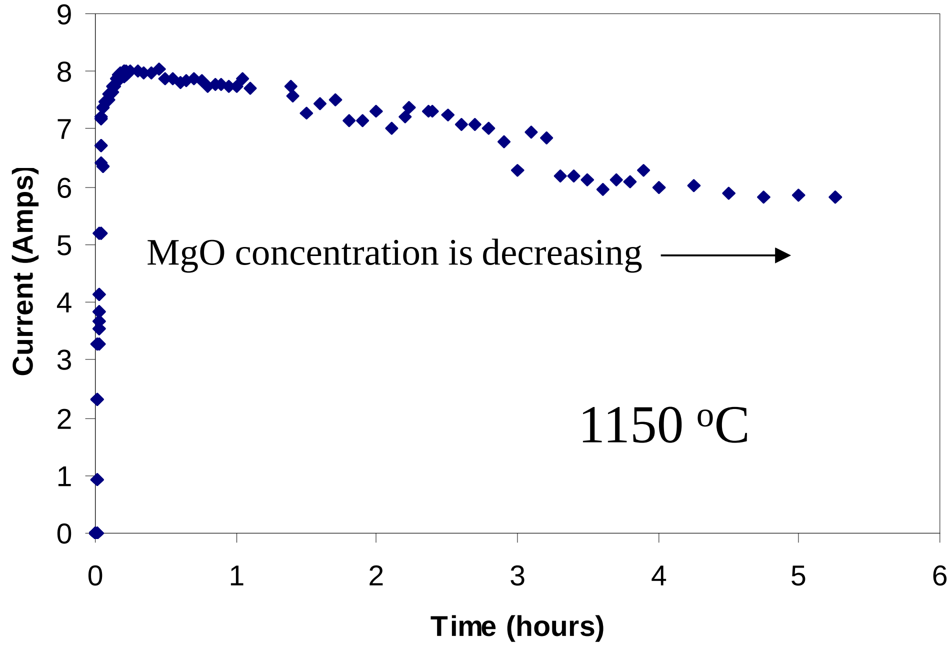
Stainless Steel construction; Single Tubular YSZ membrane;
Separate chamber for Electrolysis and Condenser; 15 g/hr of Mg at 1 Amp/cm^2; 1150 ^{o}C;
10 w% MgO in 55.5 w% MgF_2- CaF_2; Ar used as carrier and diluent for Mg vapor

Potentiodynamic Scan-Single Tube Reactor

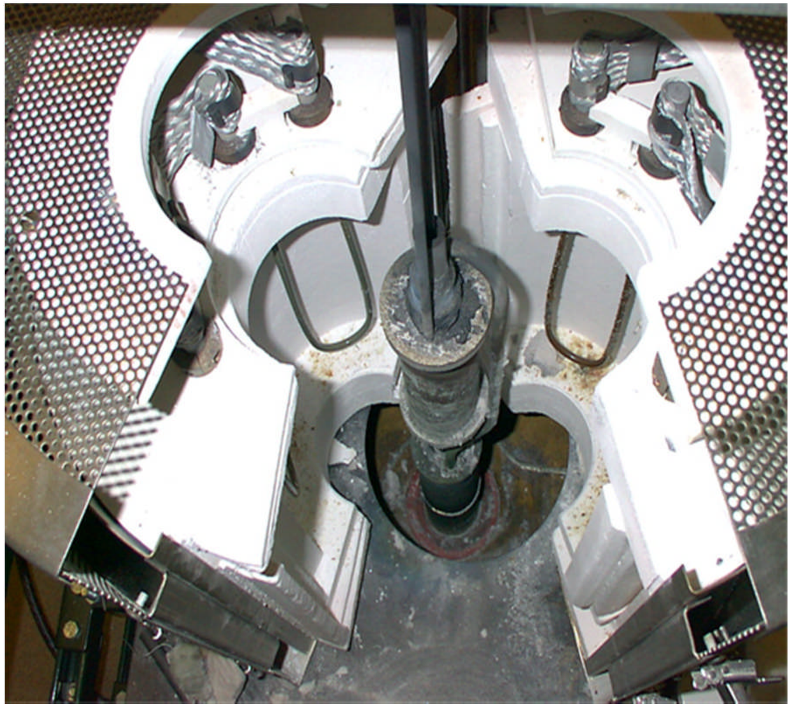


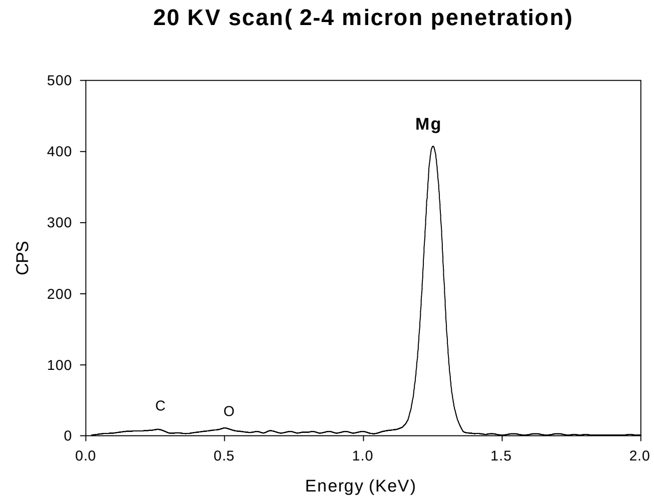
SOM Electrolysis of MgO-Single Tube Reactor

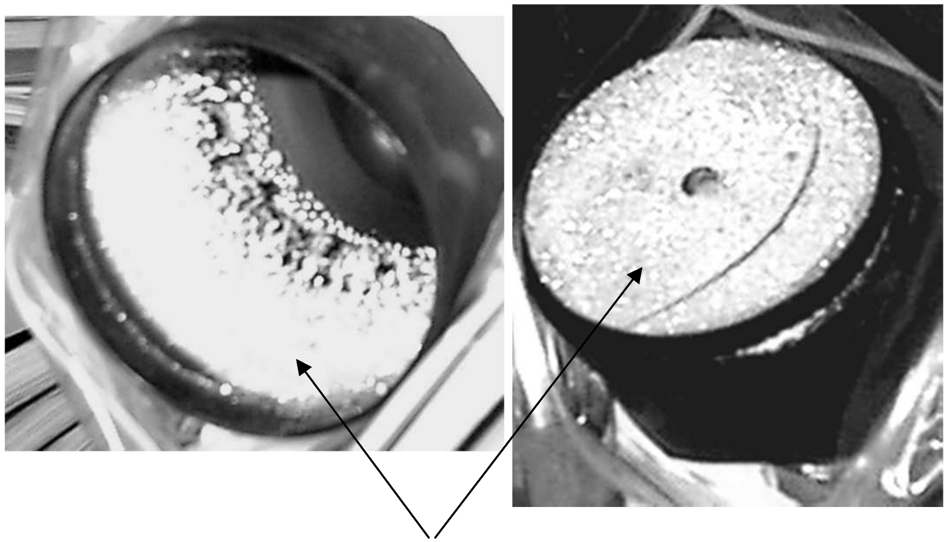
Potentiostatic Hold at 4.0 Volts



SOM Electrolysis of MgO



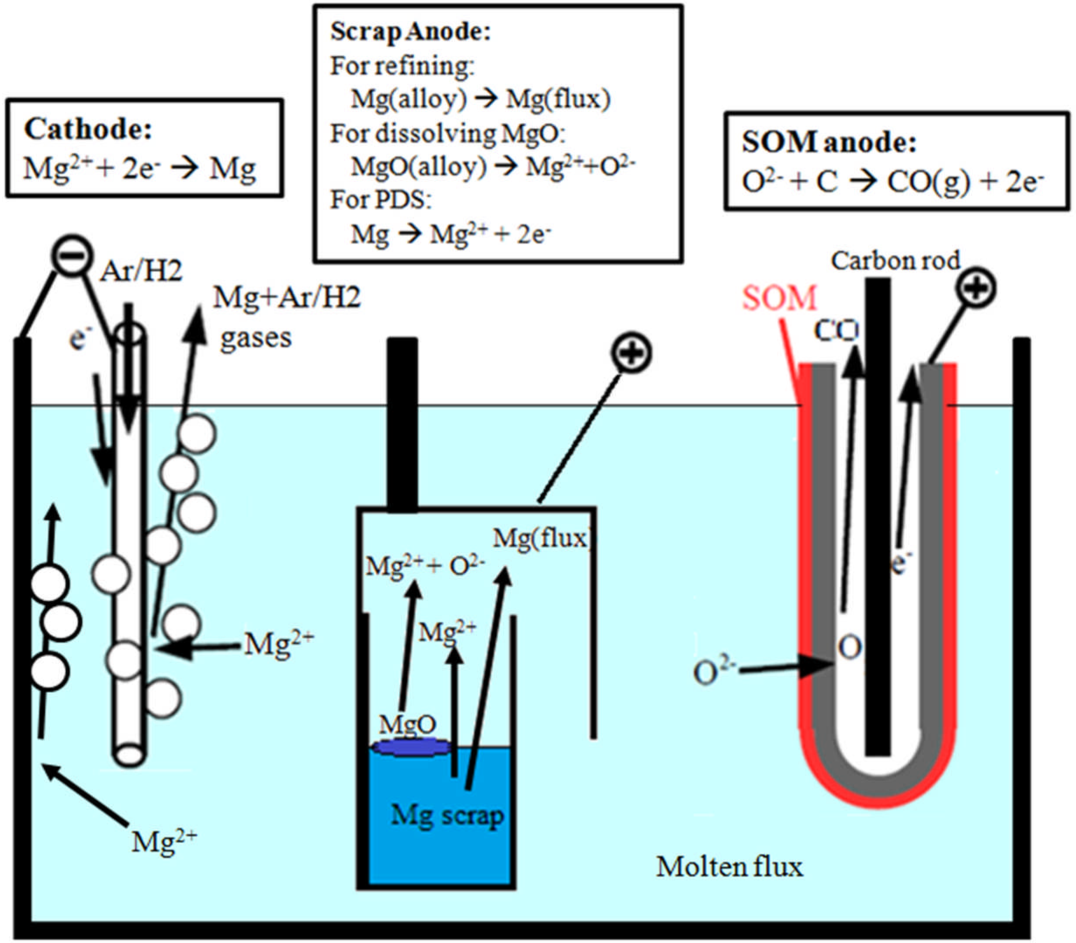




Condensed Magnesium

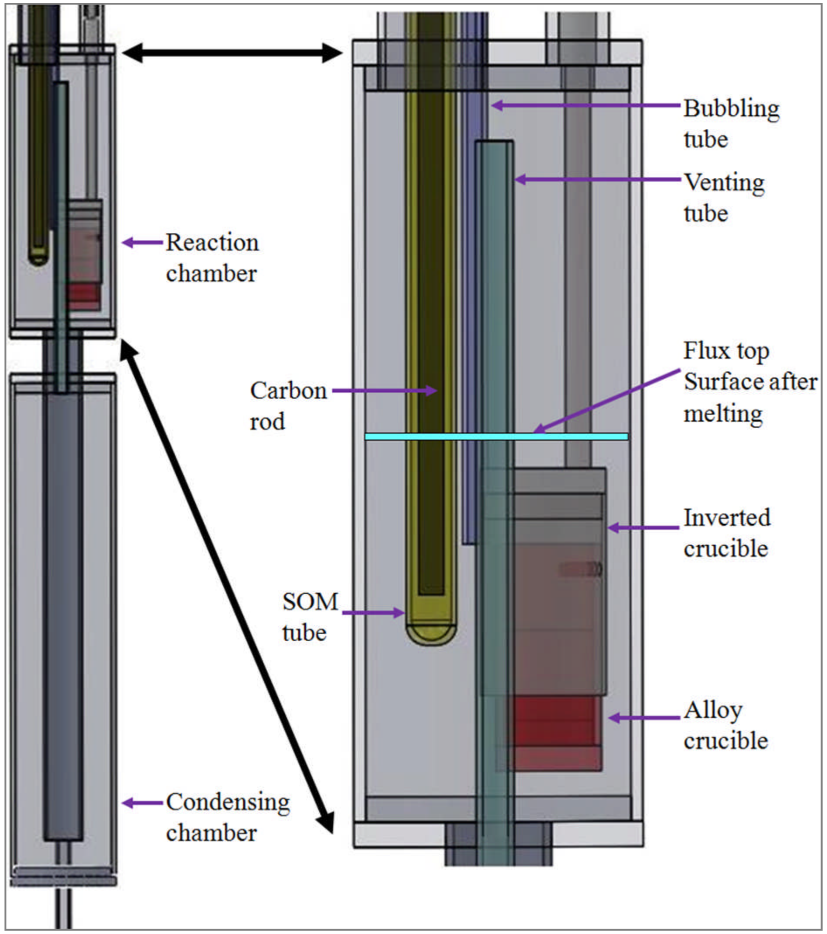
Combined SOM Electrolysis and Electrolytic Refining Processes for Recovering Magnesium from Partially Oxidized Magnesium Alloy Scrap

- Dissolve magnesium and its oxide from scrap into the flux, followed by cathodic deposition and vapor phase removal of magnesium



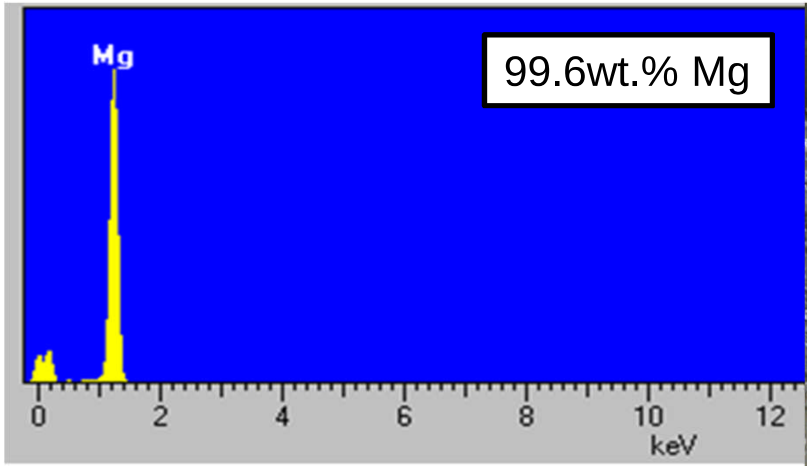
Magnesium Recovery from Partially Oxidized AZ91 Magnesium Alloy (90 w% Mg, 9 w% Al, 1 w% Zn): Combined SOM Electrolysis and Electrolytic Refining Process

Schematic of the setup:

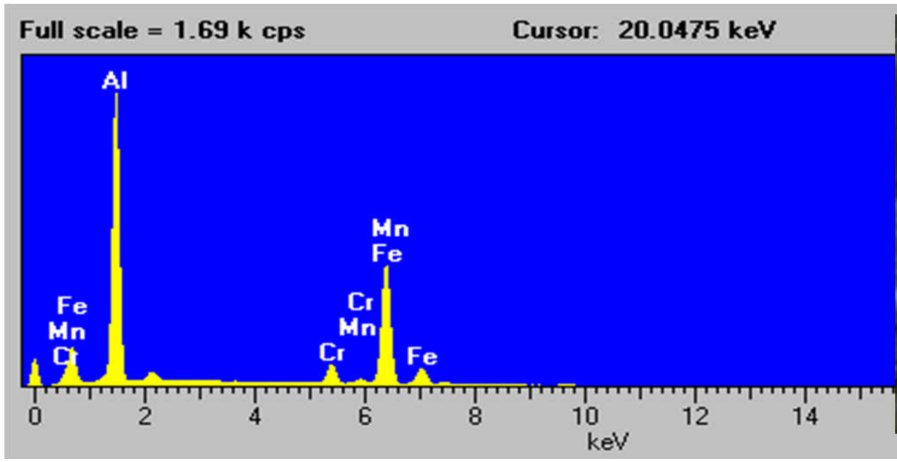


Energy-dispersive X-ray spectroscopy (EDS): Recovered Magnesium from the Scrap AZ91 Alloy

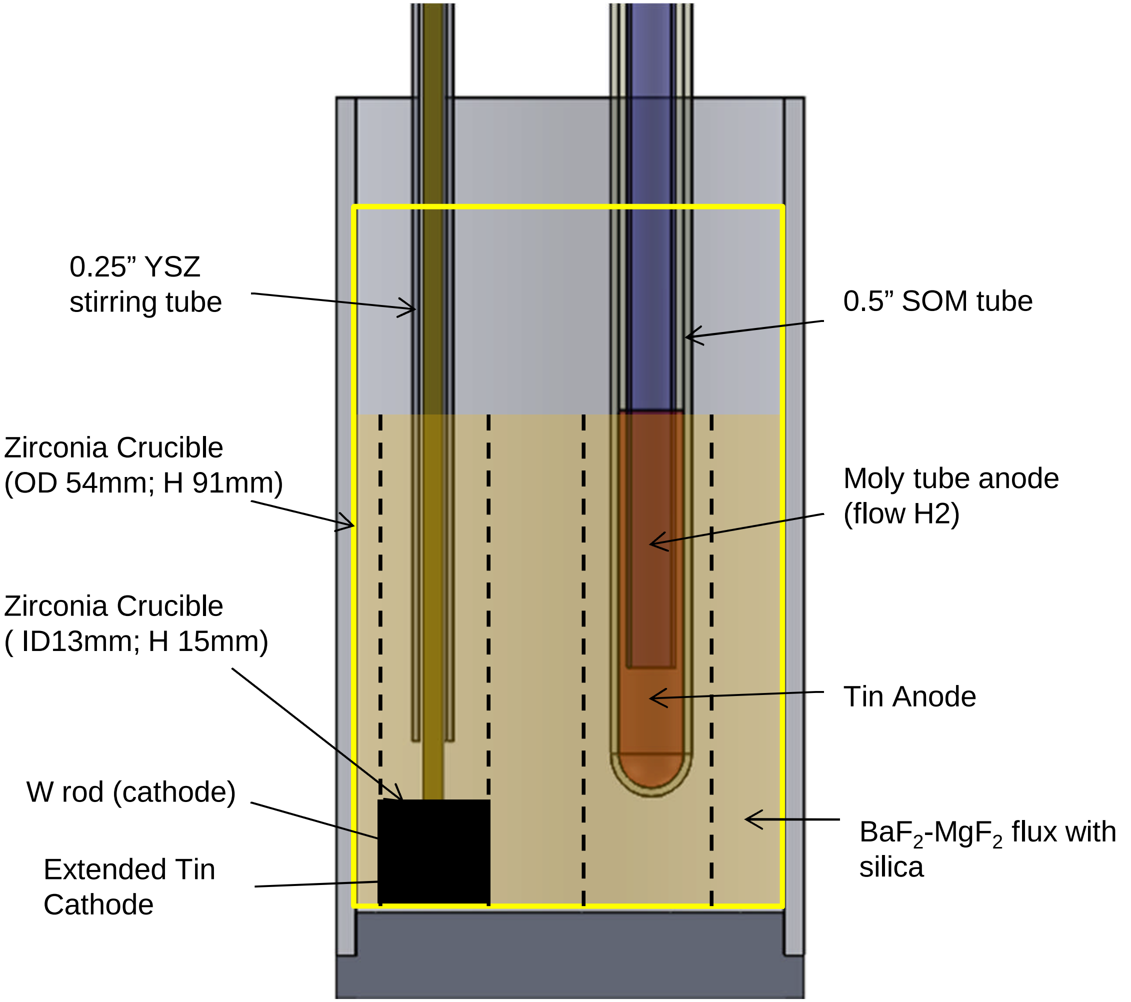
- Recovered magnesium in the condenser



- Scrap alloy residue

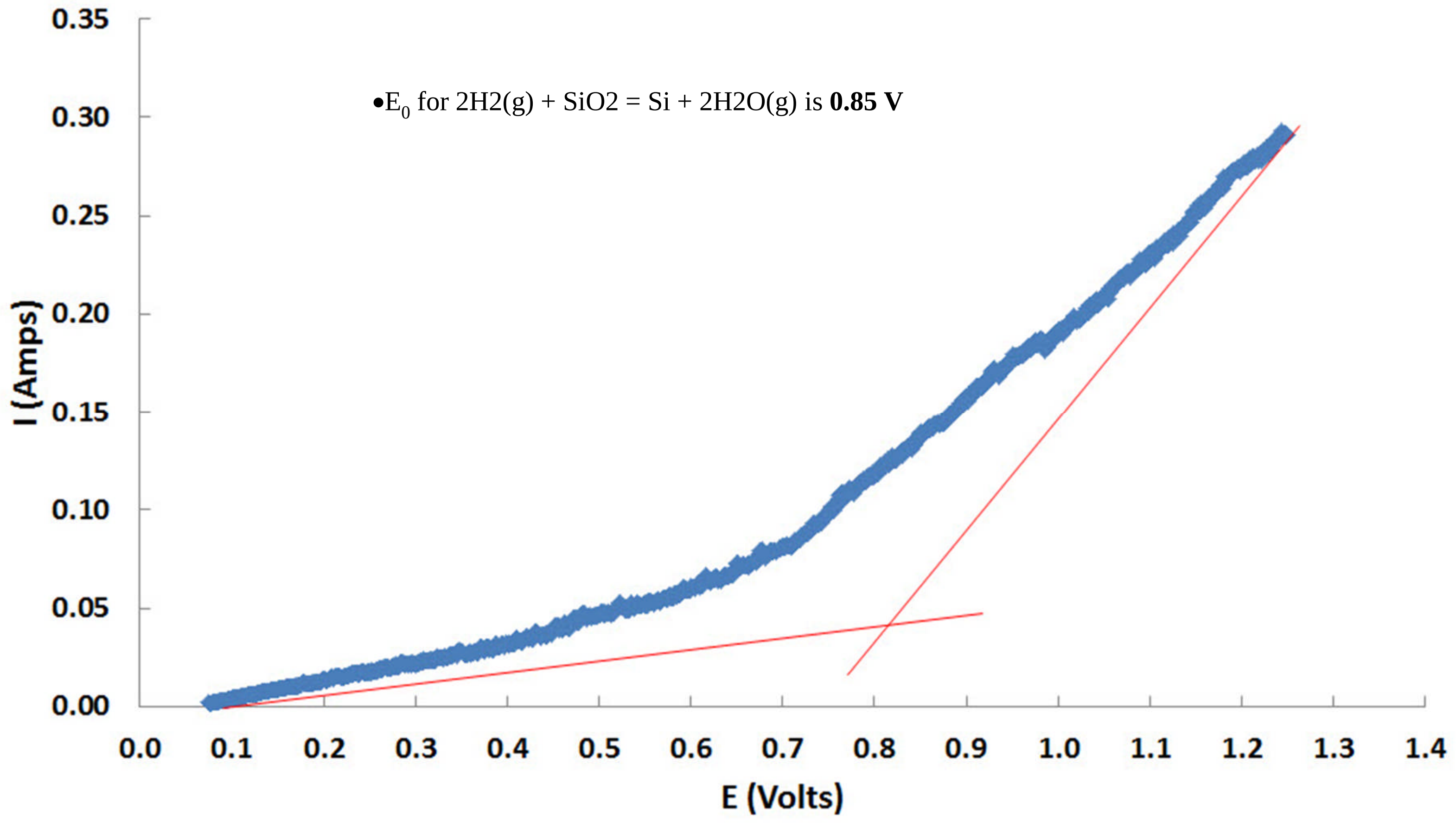


Schematic of Setup for Si-SOM Experiments

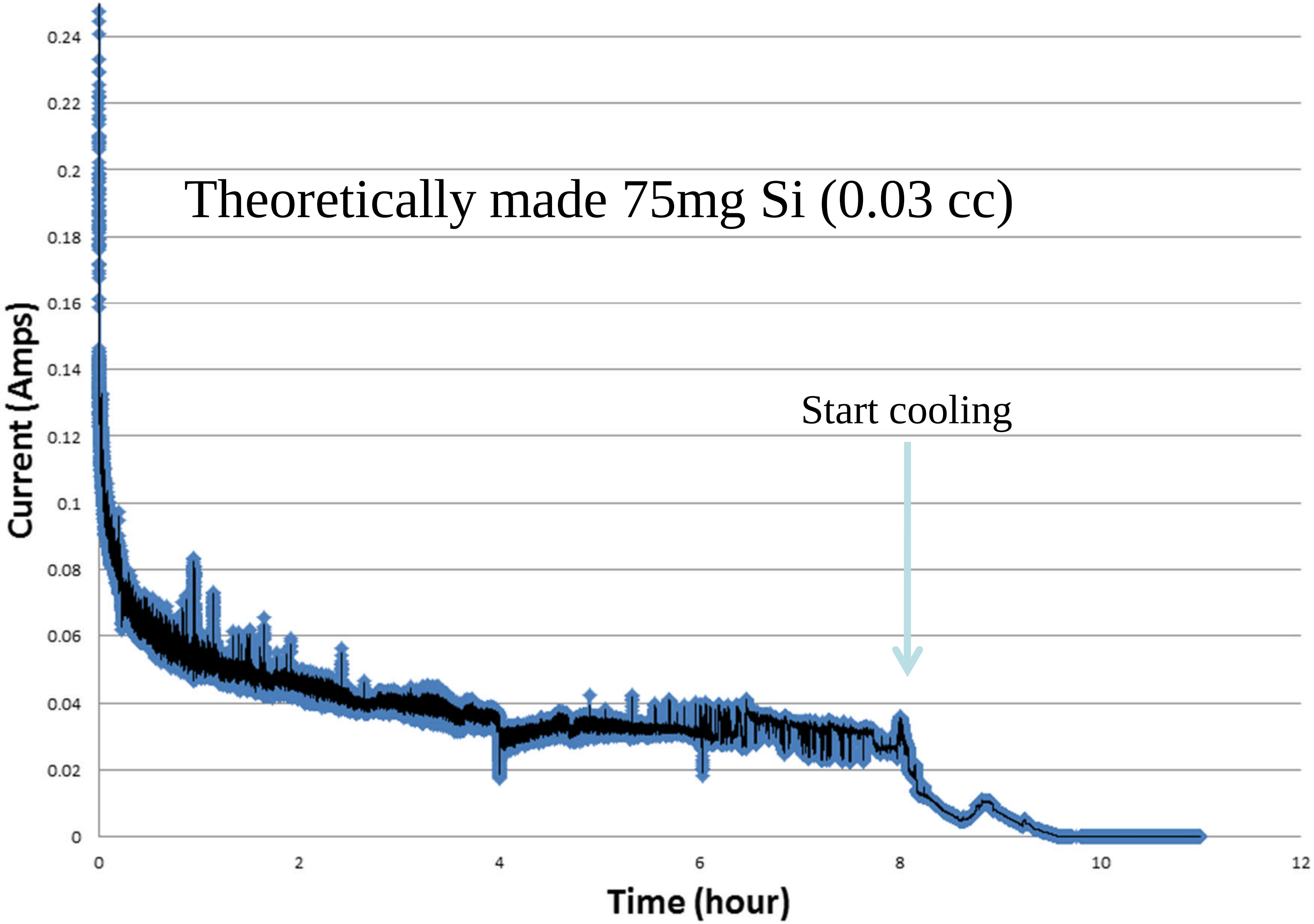


- Operating temperature 1070 C
- Si deposit was found on the surface of Tin cathode

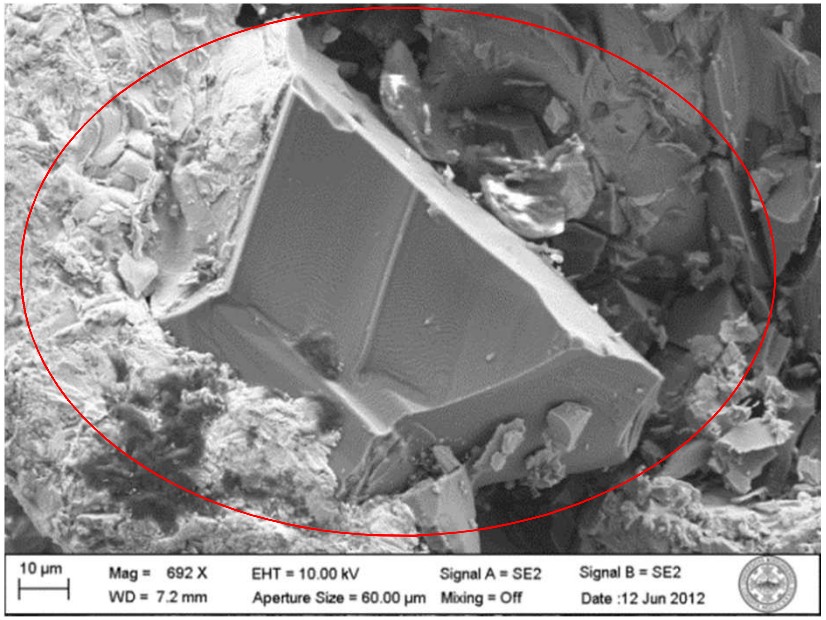
Current-voltage relationship for Silica Dissociation

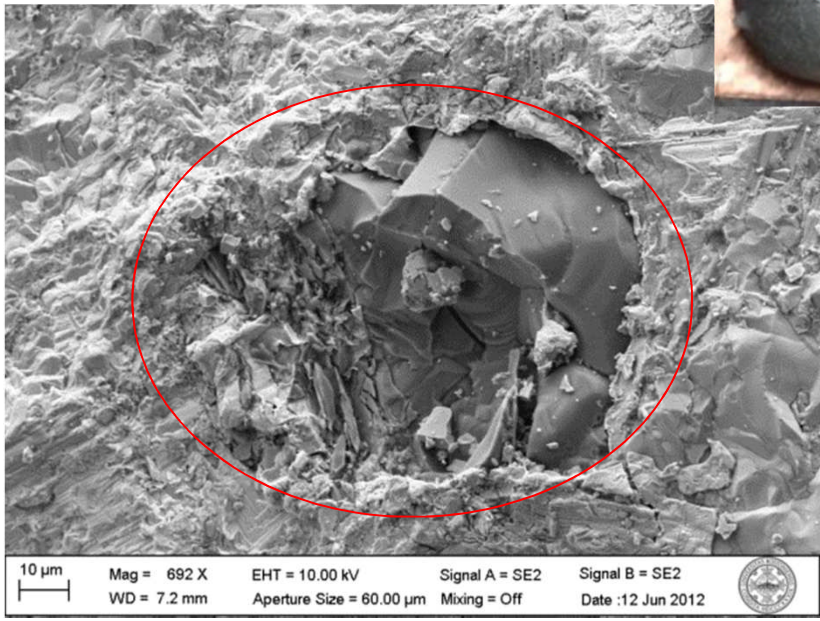


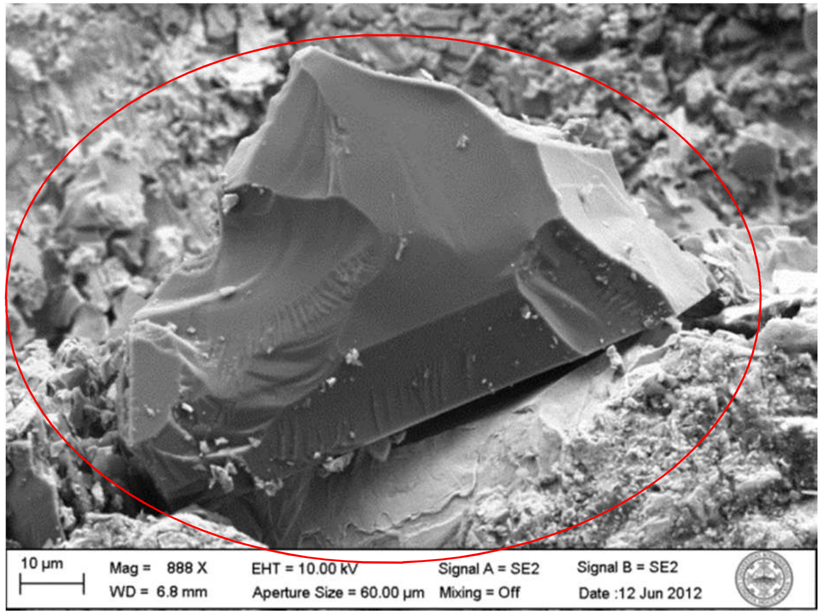
Potentiostatic

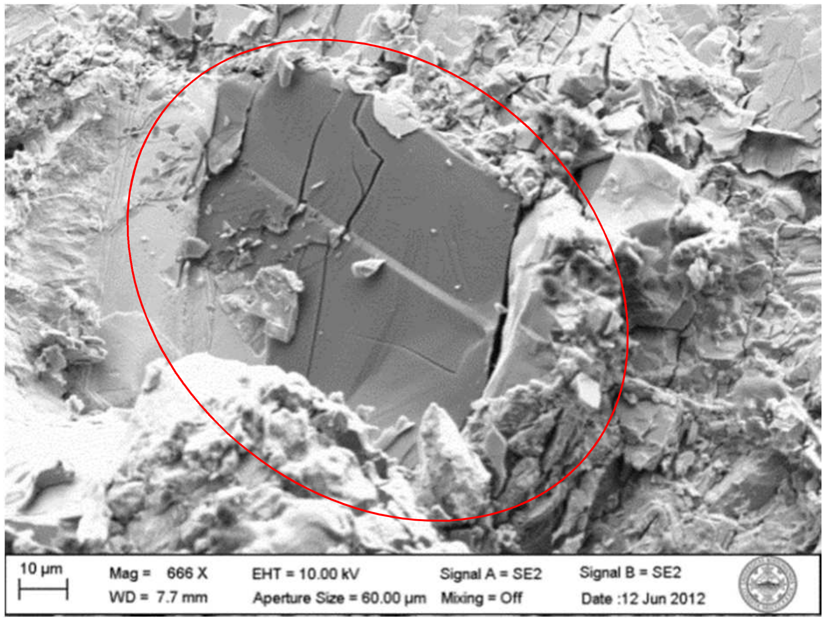


SEM image of Si deposits (Sn surface)

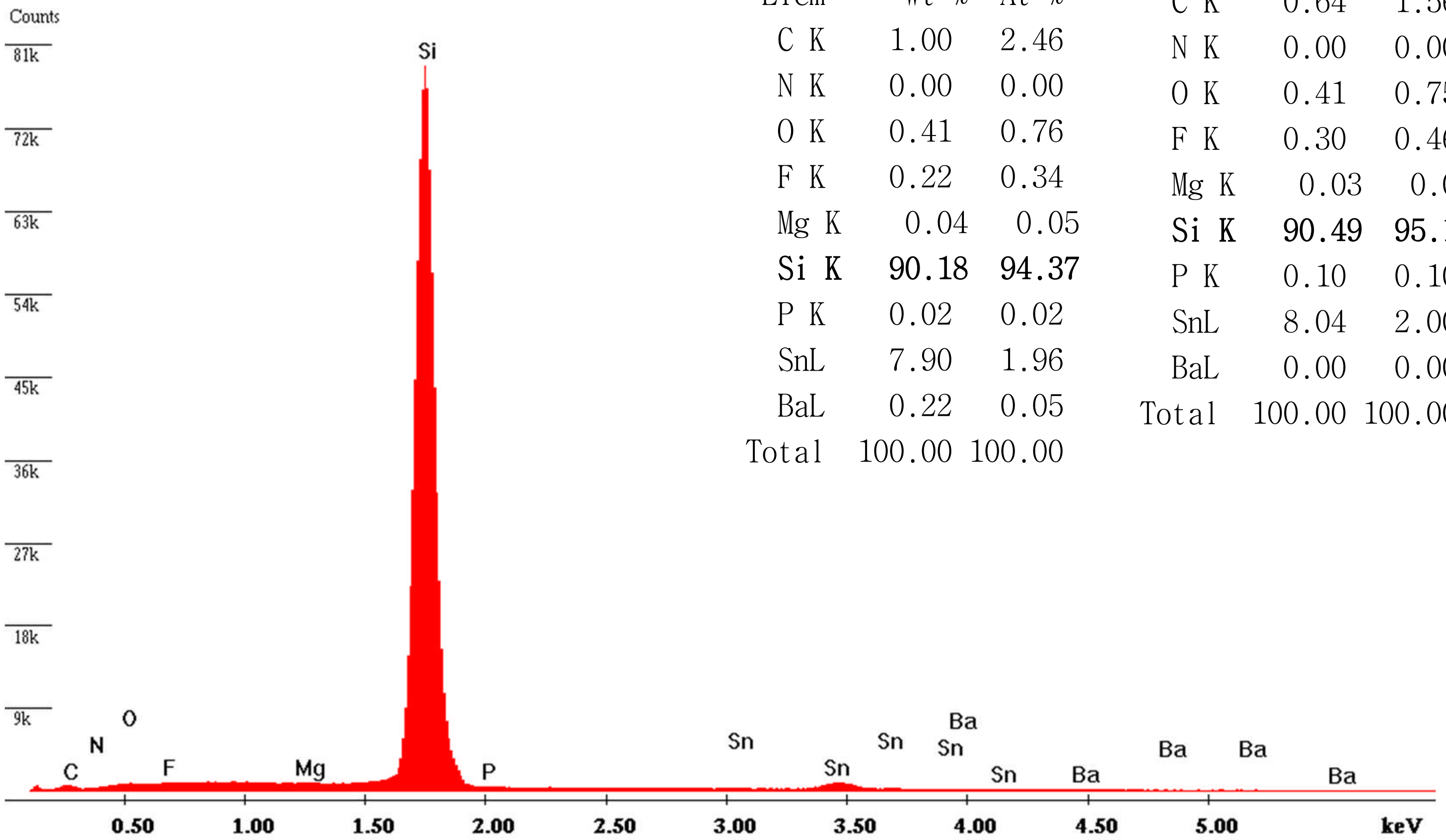








Label A:



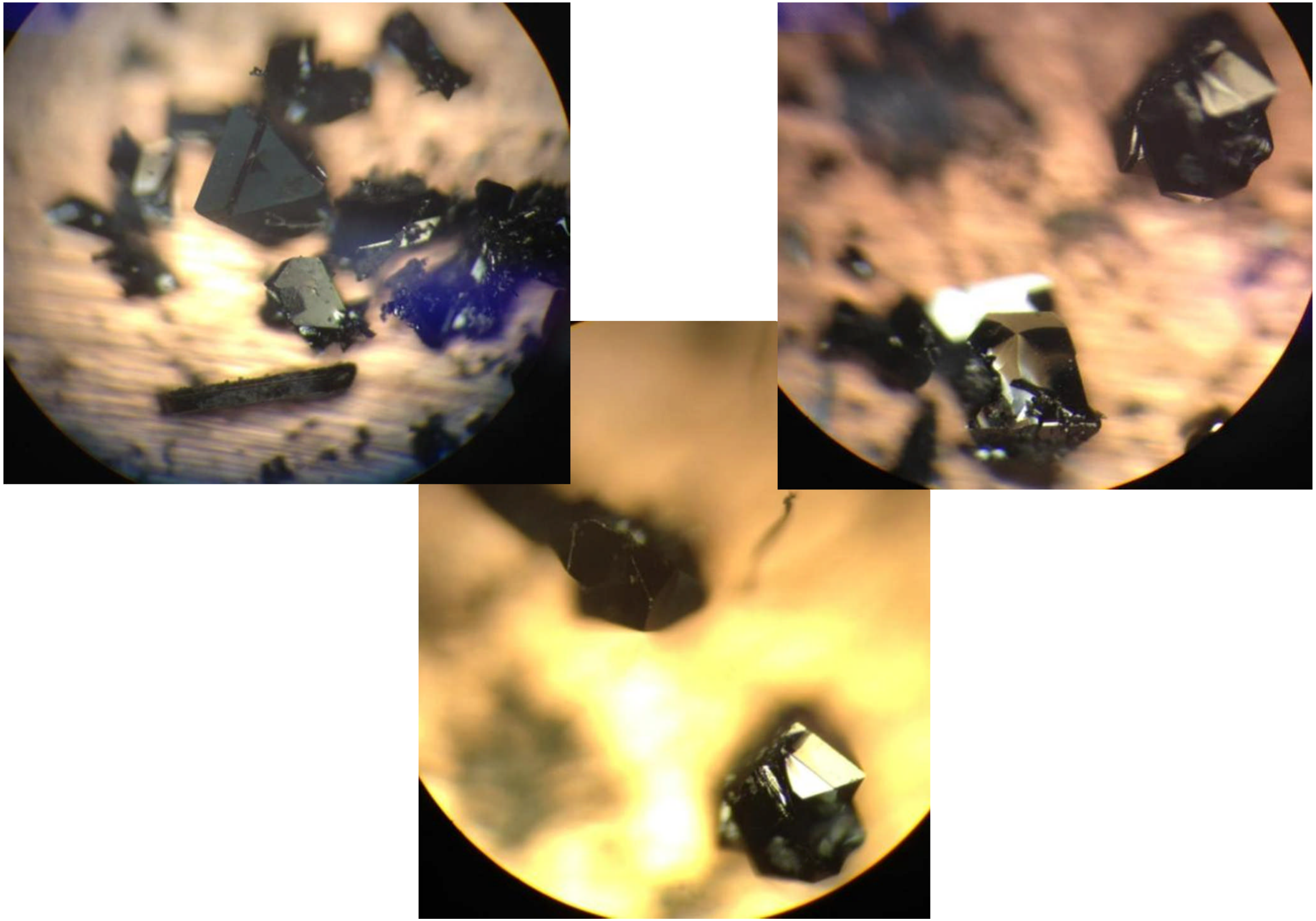
EDAX ZAF Quantification
(Standardless)
Element Normalized
SEC Table : Default

Elem	Wt %	At %
C K	1.00	2.46
N K	0.00	0.00
O K	0.41	0.76
F K	0.22	0.34
Mg K	0.04	0.05
Si K	**90.18**	**94.37**
P K	0.02	0.02
SnL	7.90	1.96
BaL	0.22	0.05
Total	100.00	100.00

Zoom in

Elem	Wt %	At %
C K	0.64	1.56
N K	0.00	0.00
O K	0.41	0.75
F K	0.30	0.46
Mg K	0.03	0.03
Si K	**90.49**	**95.10**
P K	0.10	0.10
SnL	8.04	2.00
BaL	0.00	0.00
Total	100.00	100.00

Extracted Si After Complete Etching from Sn (100x)



Selection of Ytterbium as a Surrogate for Uranium

At. No.	Element (M)	Valence	Atomic Radius (pm)	Electrons Per shell	Melting /Boiling point of fluorides (C)				
					MF2	MF3	MF4	MF5	MF6
92	Uranium (mp-1132 C) (bp-4129 C)	2,3,4,5,6	156	2,8,18,32,21,9,2 (f block)		1427 and 1977	1036 and 1417	327 and 727	64.05 (TP)
70	**Ytterbium (mp-824 C) (bp-1193 C)**	**2,3**	**176**	**2,8,18,32,8,2 (f block)**	**1052 and 2380**	**1157 and 2263**			
58	Cerium (mp-798 C) (bp-3443 C)	3,4	181	2,8,18,19,9,2 (f block)		1430 and 2327	977 and 1727		
63	Europium (mp-826 C) (bp-1529 C)	2,3	180	2, 8, 18, 25, 8, 2 (f block)	1298 and 2427	1276 and 2277			
73	Tantalum (mp-3014 C) (bp-5453 C)	3,4,5	147	2,8,18,32,11,2 (d block)	1237 and 1977	1477 and 2077		95 and 229	
22	Titanium (mp-1668 C) (bp-3287 C)	2,3,4	147	2,8,10,2 (d block)	1277 and 2152	1200 and 1400	377		

Fluoride Flux Preparation

Thermogravimetry DTA Measurements

$LiF–YbF_3$ (concl.)

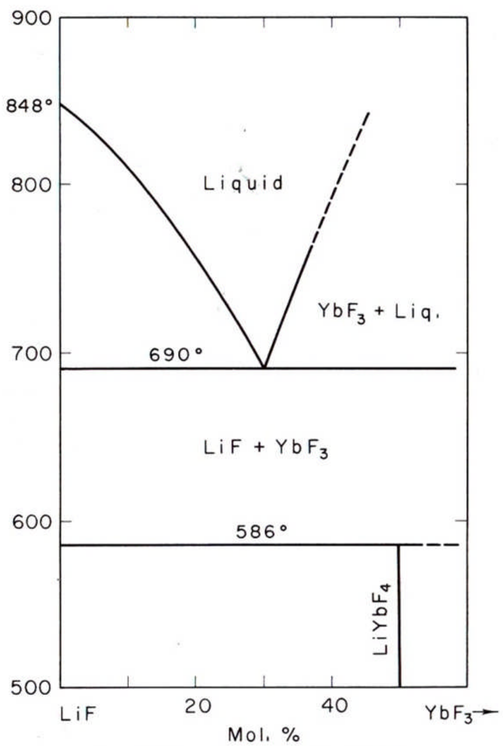
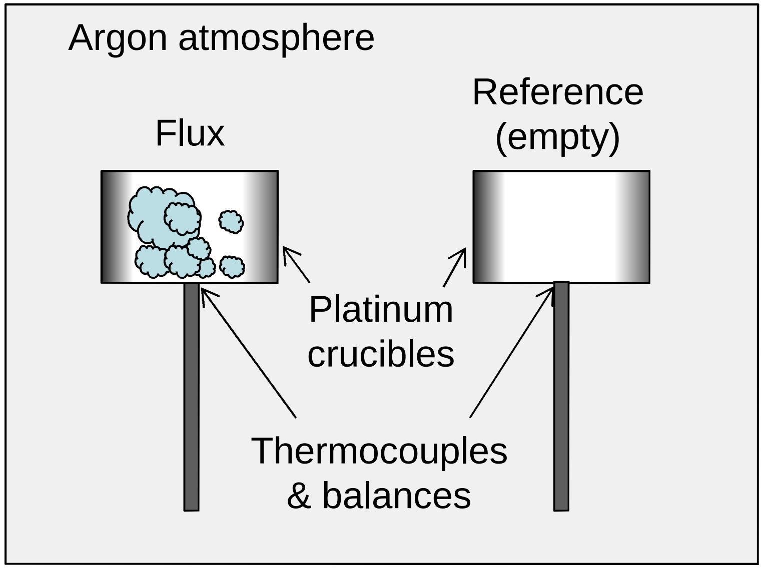


FIG. **3379.**—System $LiF–LiYbF_4$.

G. A. Bukhalova and E. P. Babaeva, *Zh. Neorgan. Khim.*, 11 [3] 624 (1966); *Russ. J. Inorg. Chem.* (*English Transl.*), 339 (1966).

$LiF-YbF_3-Yb_2O_3$
- 0 w% Yb_2O_3
- 2 w% Yb_2O_3
- 5 w% $Yb_2O_3$3
- 10 w% Yb_2O_3

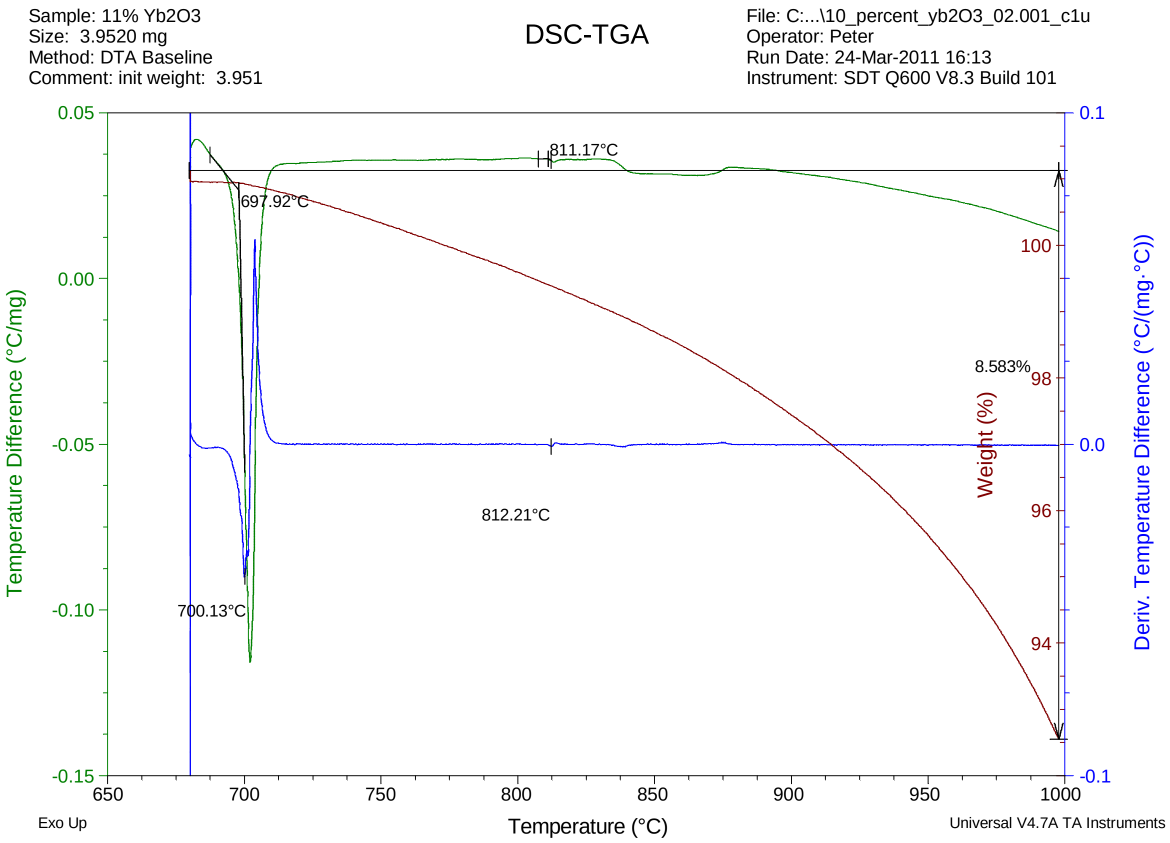
Mix, melt and quench 70 mole%LiF–30mole% YbF_3 with desired amounts of Yb_2O_3 in a controlled environment



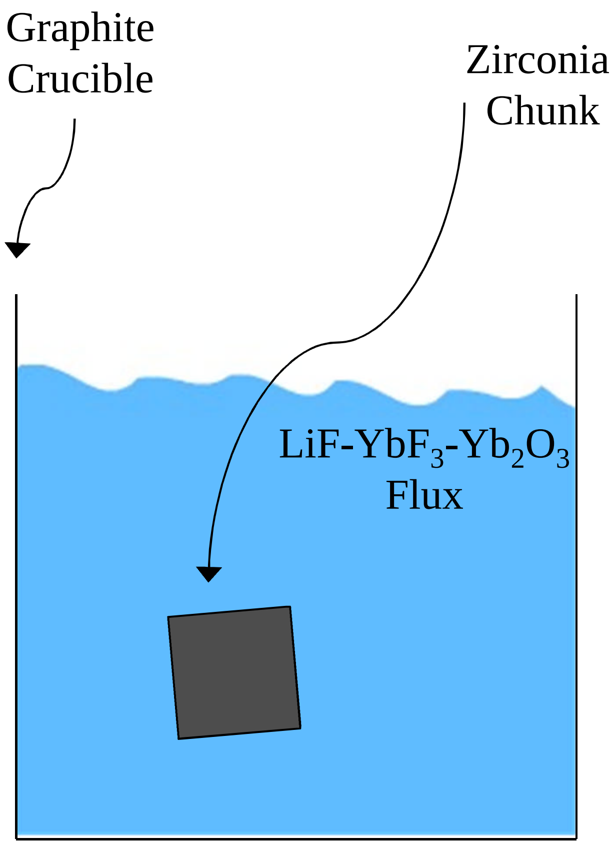
- Heat flux and reference at a constant rate to 1000 C
- Note difference in temperature and weight between flux and reference during heatup (determine liquidus)
- Cool flux and reference at a constant rate to 500 C and note difference in temperature between flux and reference (reconfirm liquidus)

DTA-TFA Data

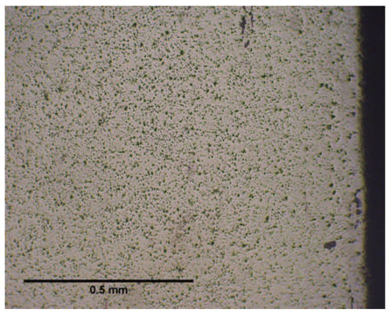
11 wt% Yb2O3 solubility in flux below 820 C (Yb melting point)



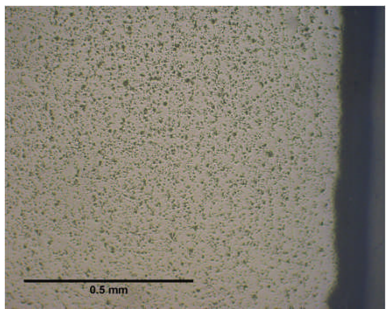
Determine Stability of YSZ Membrane in Flux



Place a chunk of YSZ membrane in the flux (LiF$_2$-YbF$_3$-Yb$_2$O$_3$) at 820 C for 5 hours



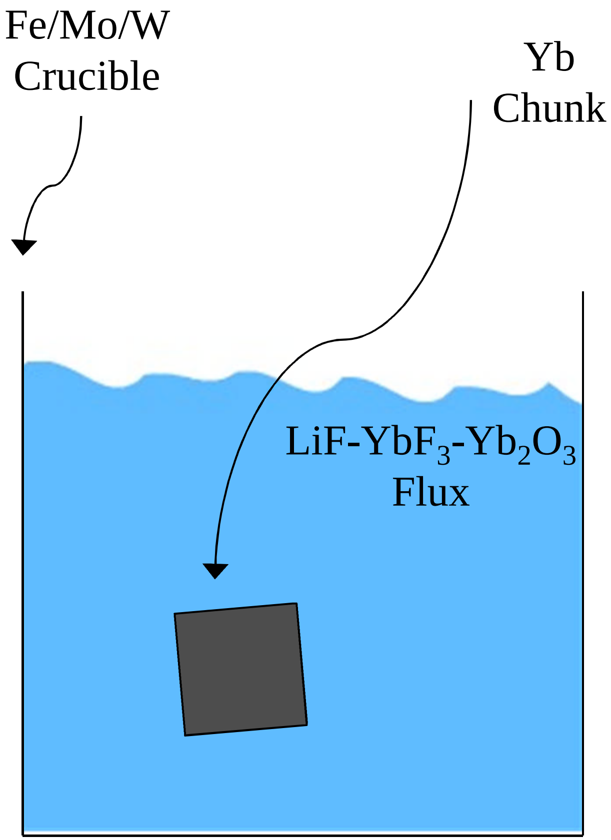
Section of
YSZ in Flux



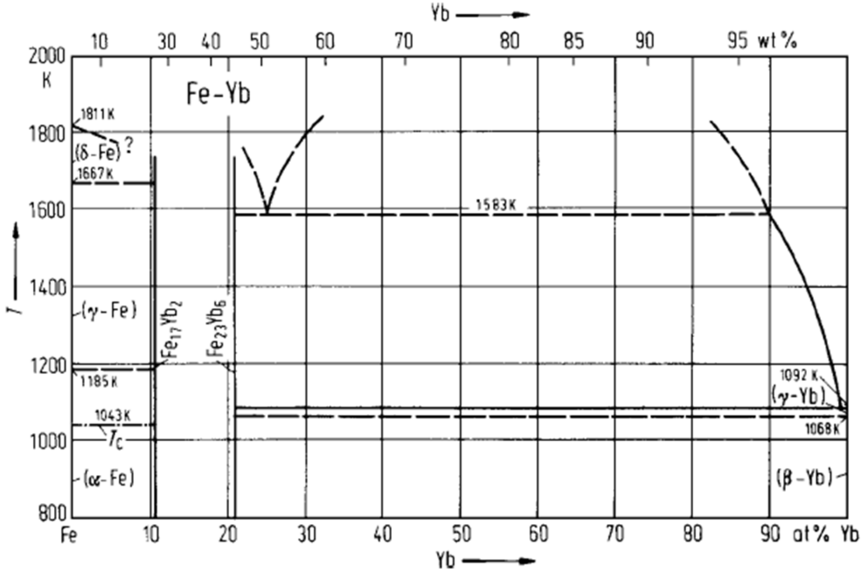
Section of
Original YSZ

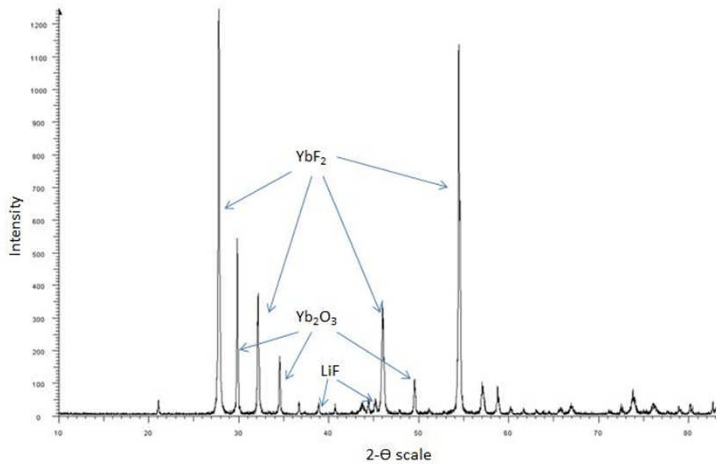
Determine Stability of Fe Crucible/Cathode with Flux and Yb

Place a chunk of Yb in the flux (LiF_2-YbF_3-Yb_2O_3) at 100 C above its liquidus in the Fe crucible for 5 hours

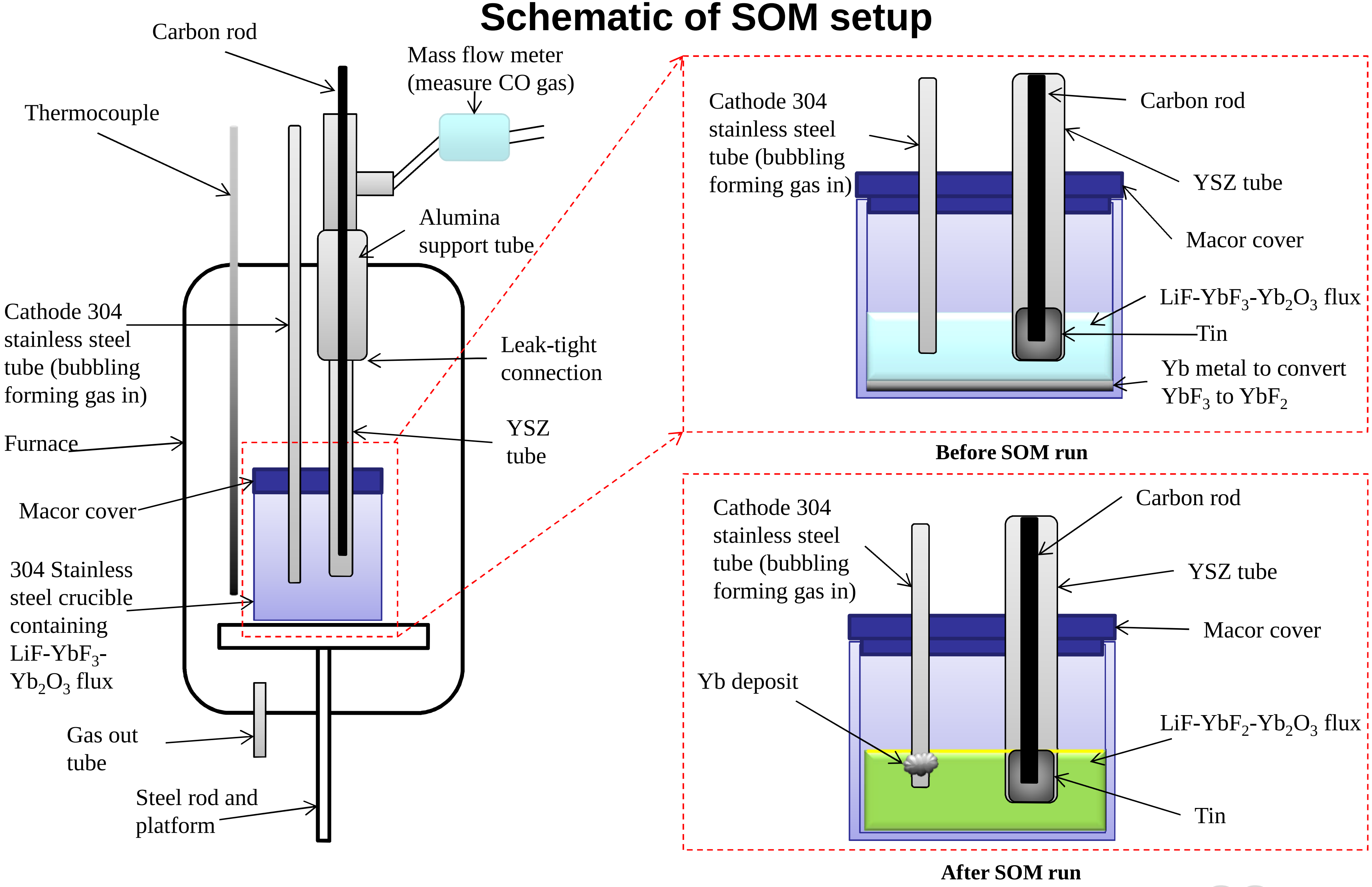


$$Yb + 2YbF_3 \rightarrow 3YbF_2$$

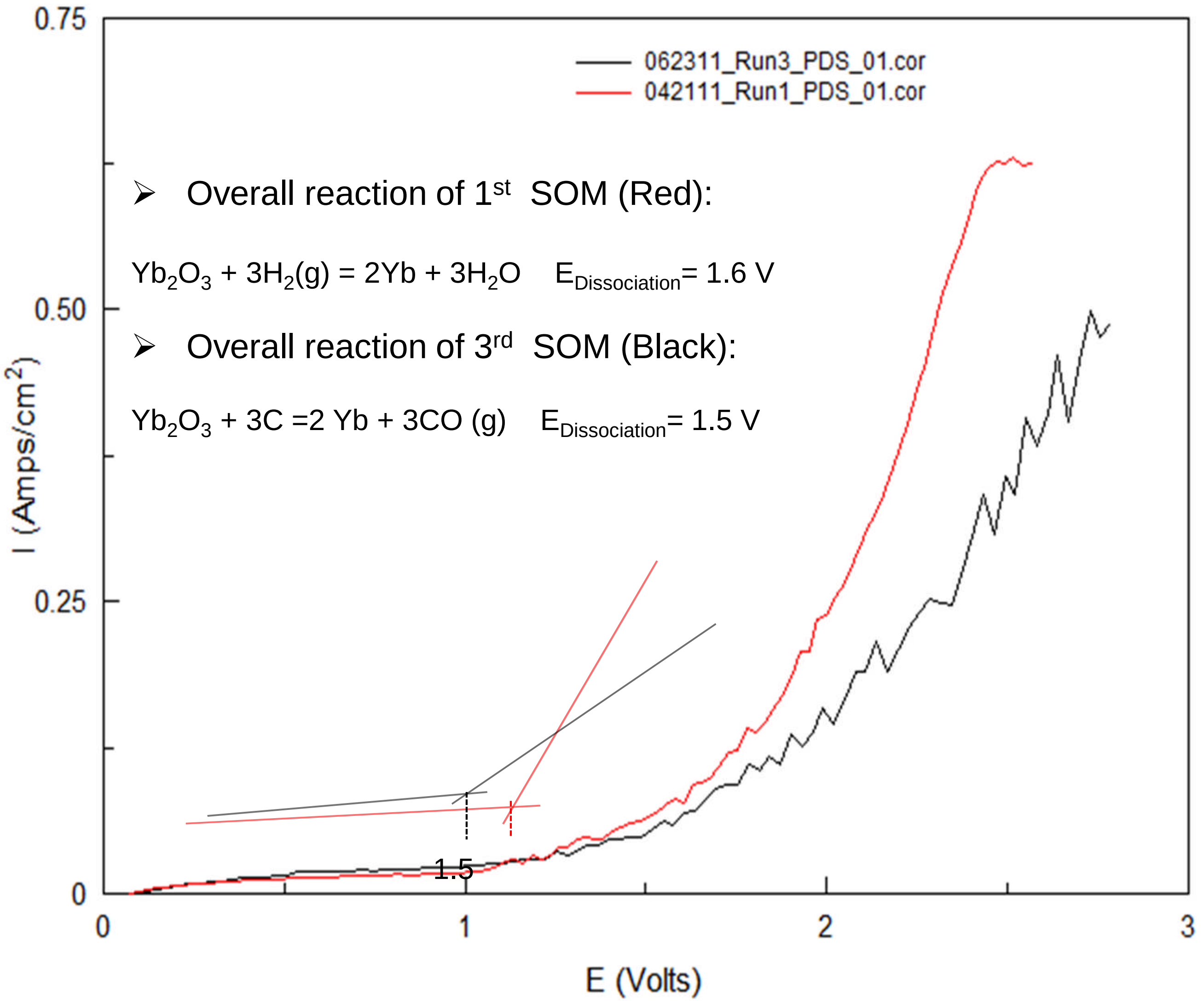




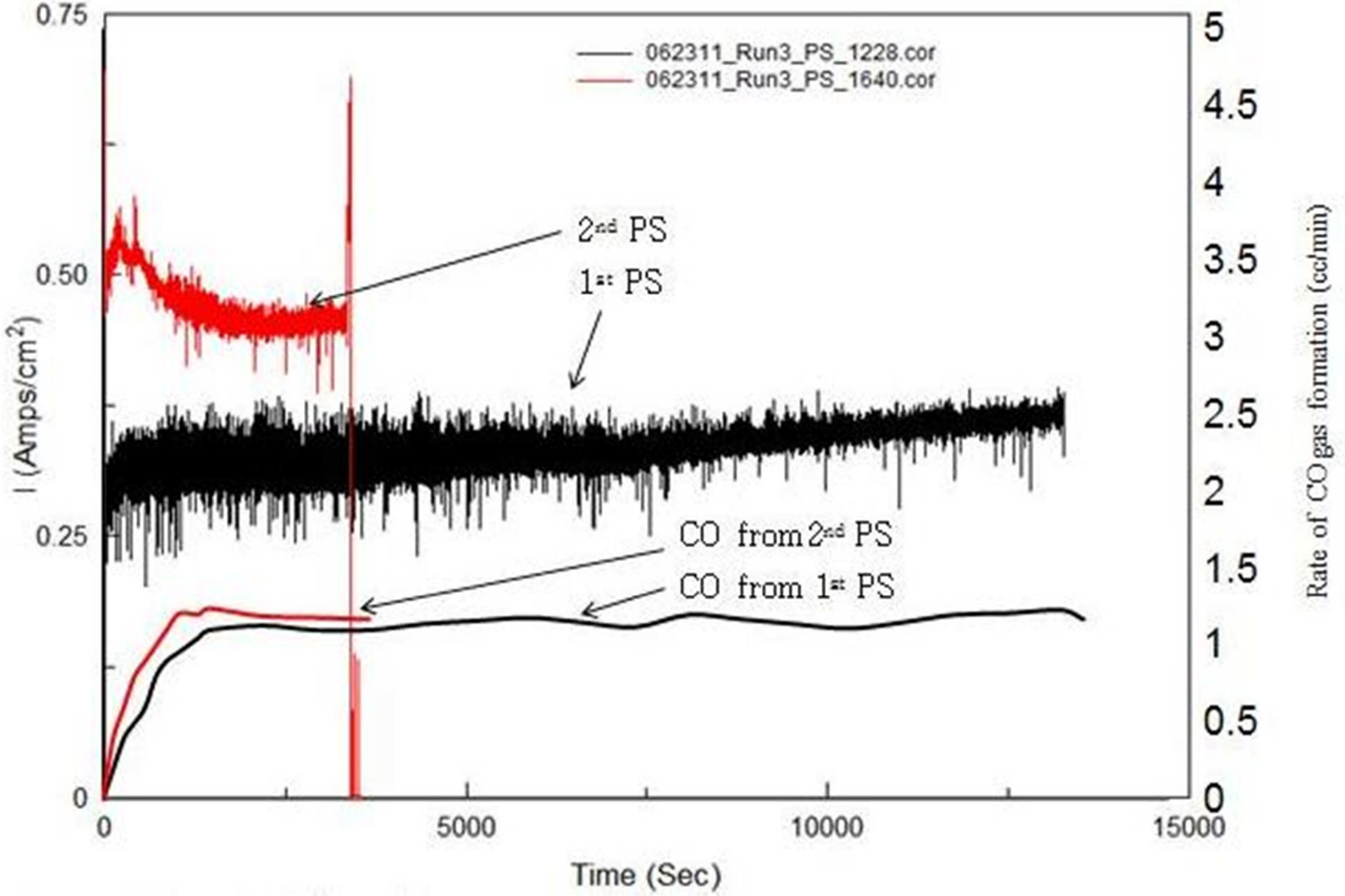
Schematic of SOM setup



Potentiodynamic scan (PDS)

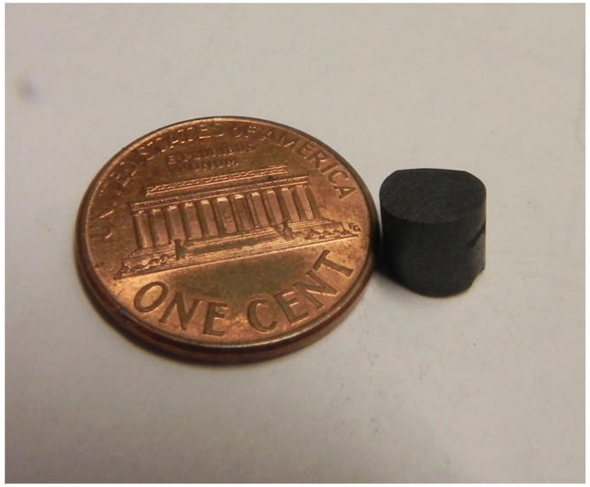


Potentiostatic Measurement and CO Evolution



Efficiency of Electrolysis

- Weight loss of carbon rod: 0.27 g



$Yb_2O_3 + 3C = 2Yb + 3CO\ (g)$

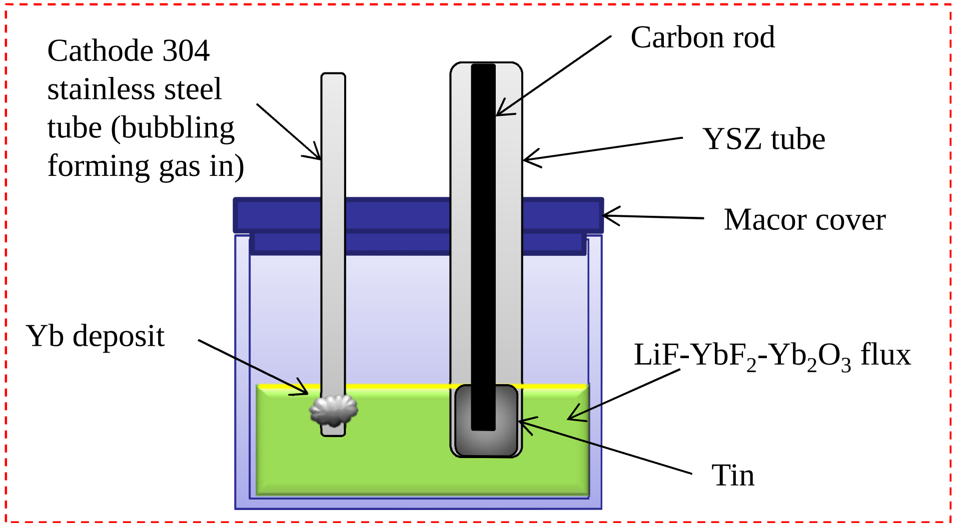
1. Assuming 100% Faradic efficiency, theoretical amount of Yb produced based on measured current : 3.24 g
2. Amount of Yb produced based on CO measurement: 2.04 g
3. Amount of Yb produced based on carbon rod weight loss : 2.60 g

Electrolysis efficiency

$$\frac{2.04}{3.24} = 63\%$$

$$\frac{2.60}{3.24} = 80\%$$

Metal Deposit on Cathode



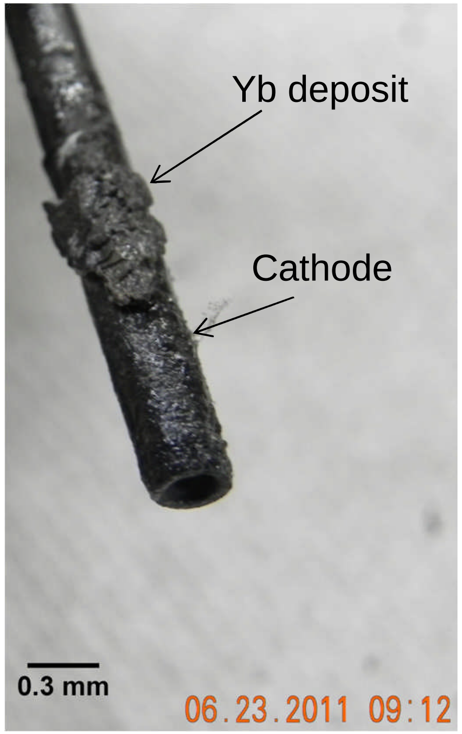
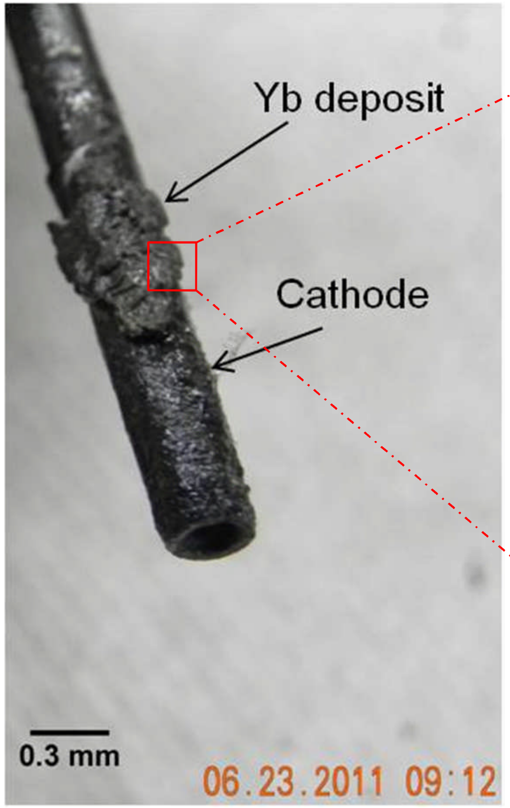


Photo of Yb deposit

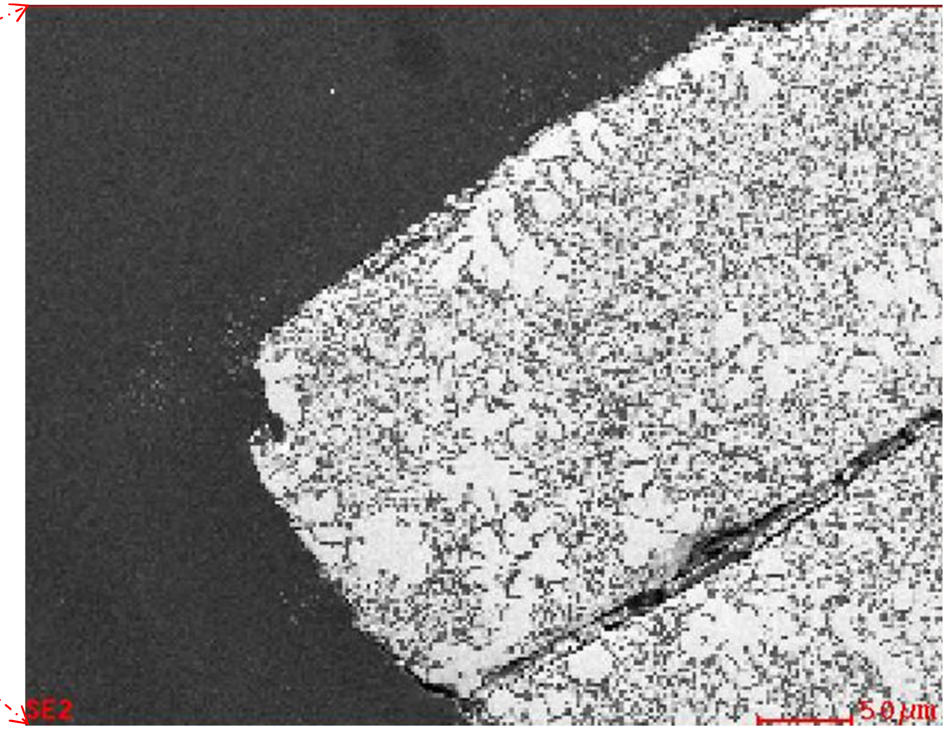
Operating temperature for SOM: 800° C

Melting point of Yb : 819 ° C

Metal Deposit on Cathode

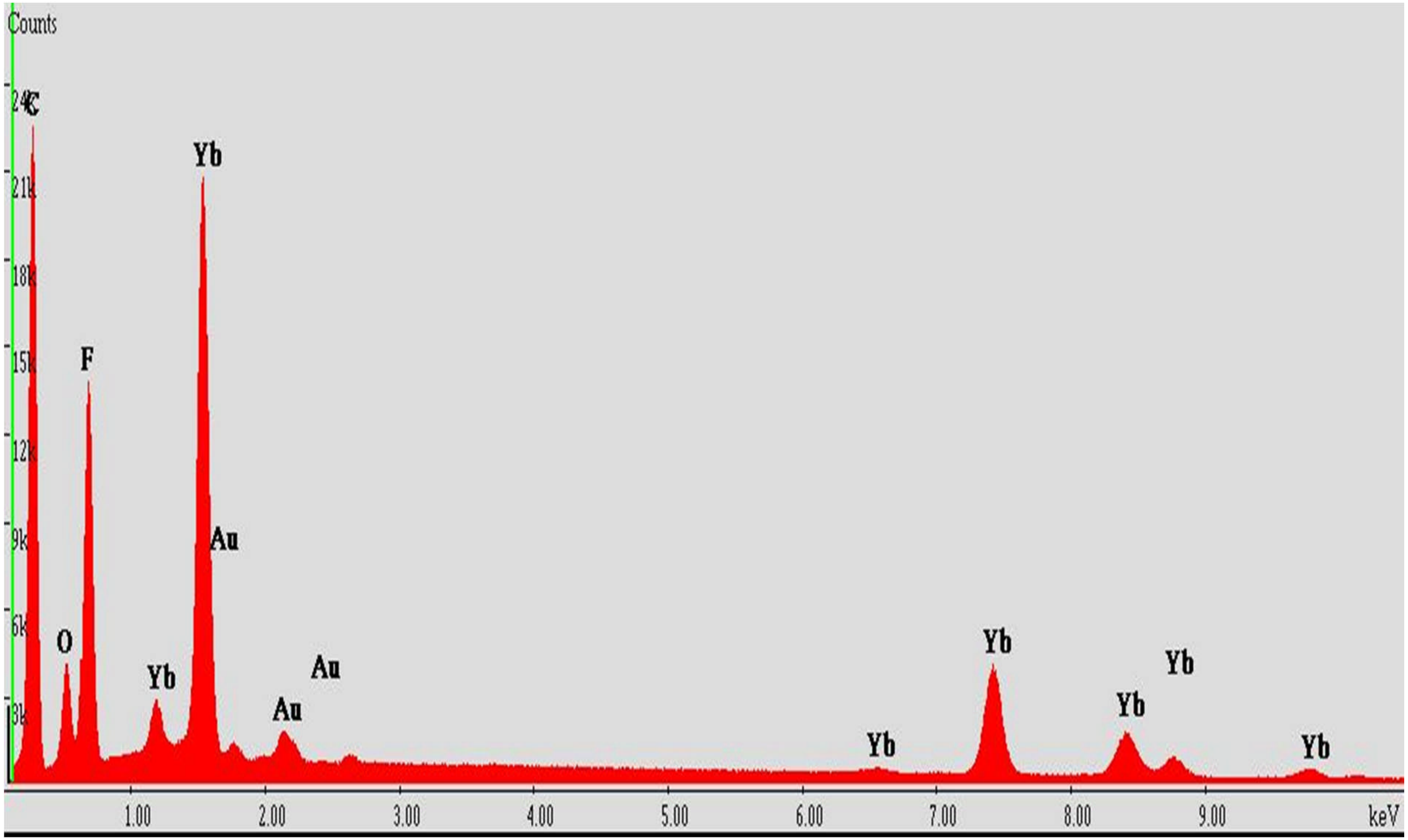


Metal deposit

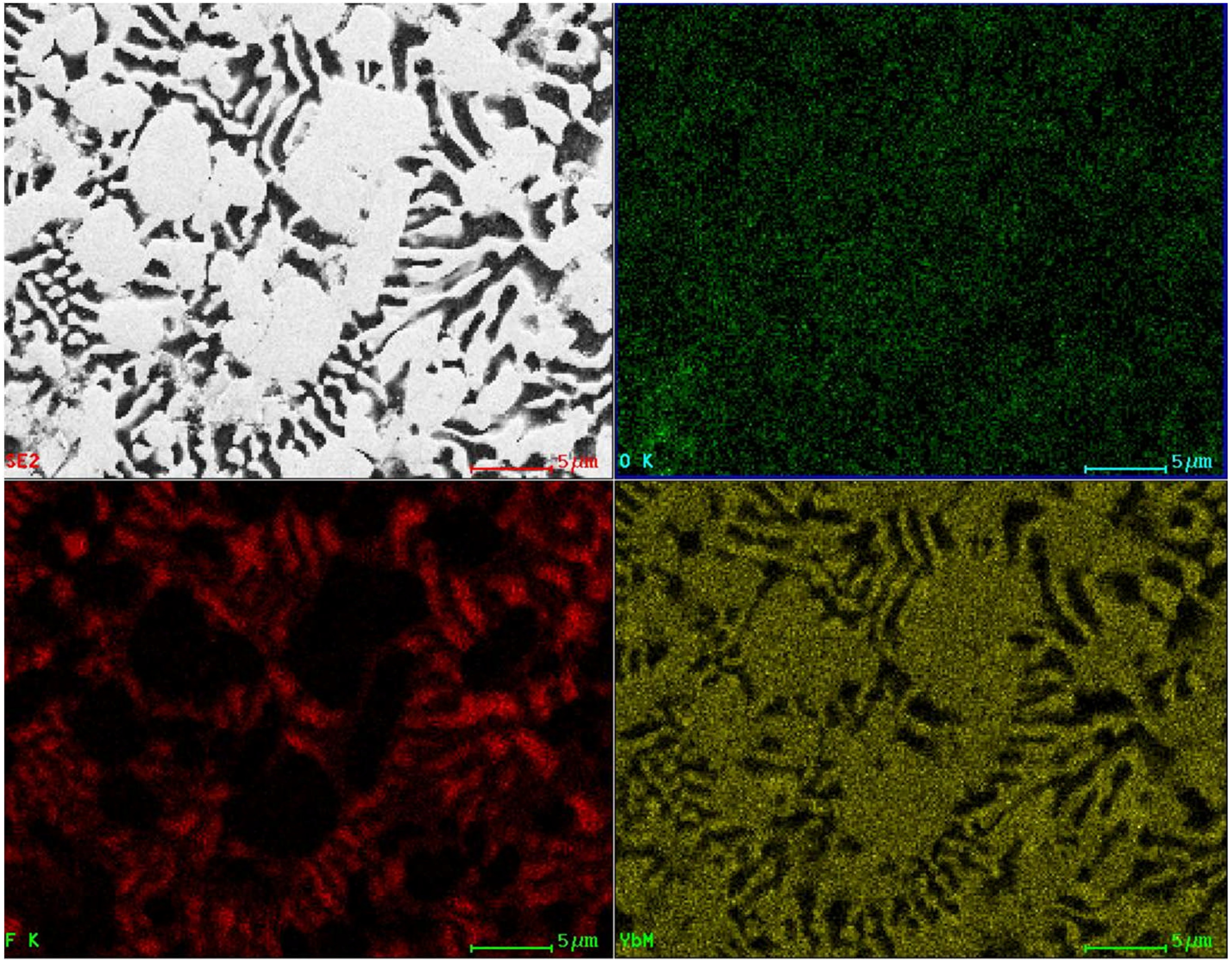


SEM Image of the Deposit

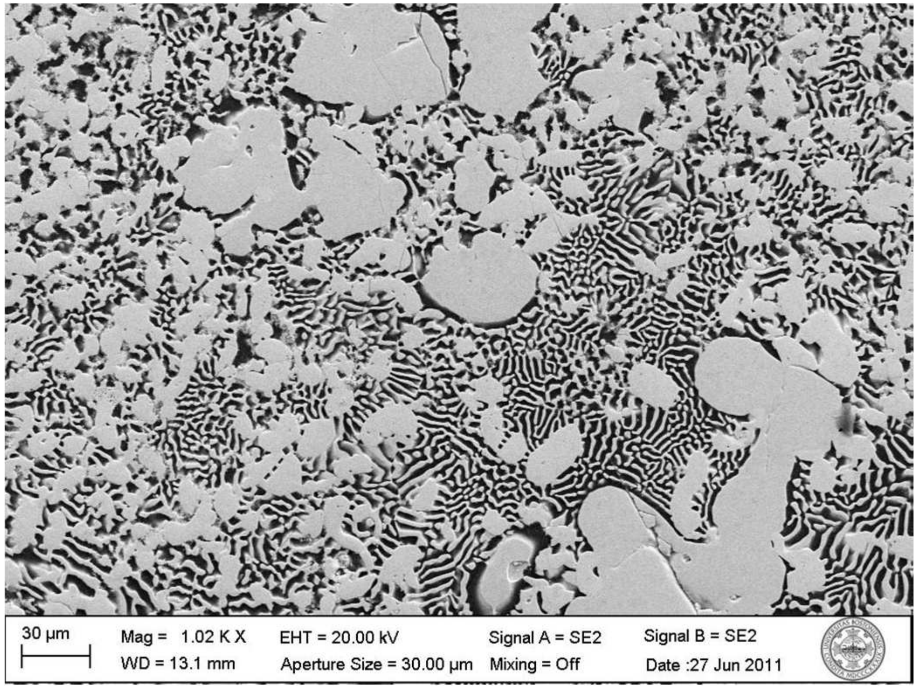
EDS Spectrum of the Metal Deposit

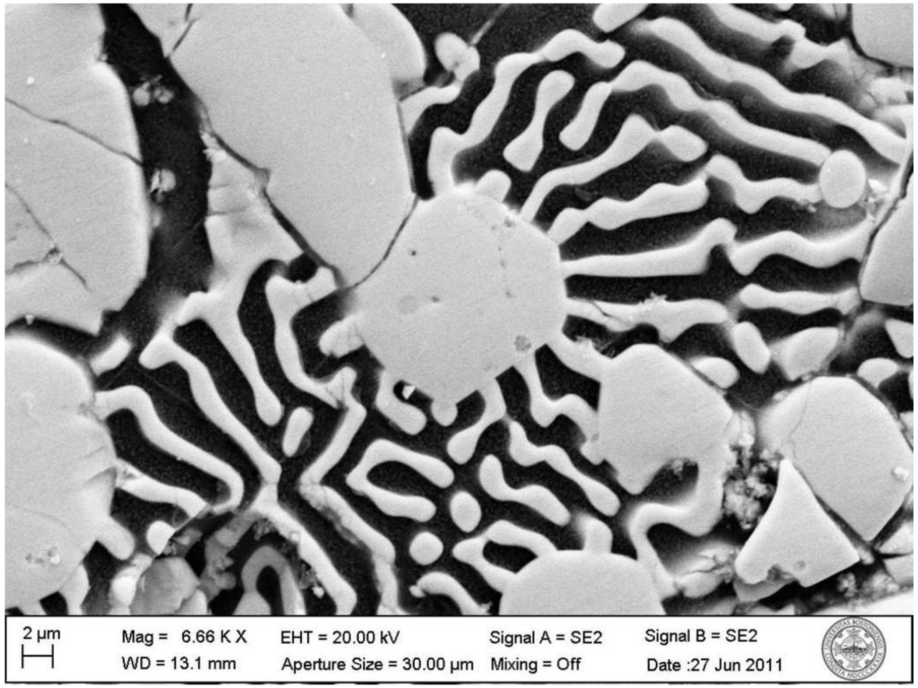


X-ray Maps confirm Yb metal deposit



SEM Image of the Deposit Under Different Magnifications

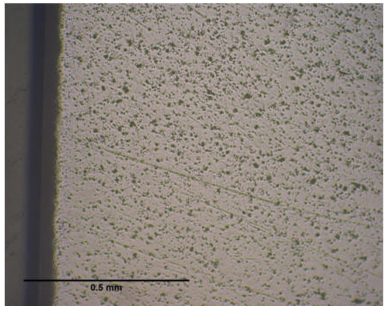


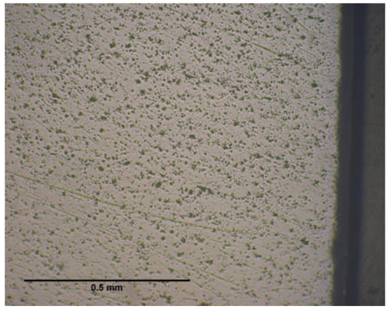


Stability of YSZ Tube During SOM Electrolysis

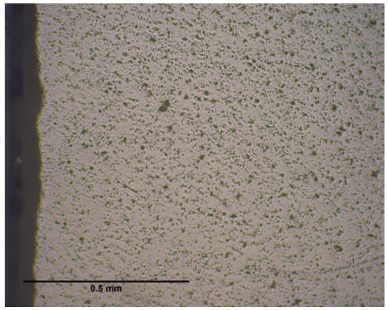
Inside part | Outside part

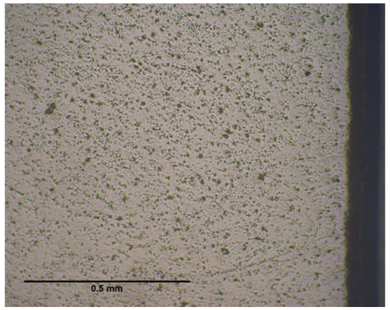
Original



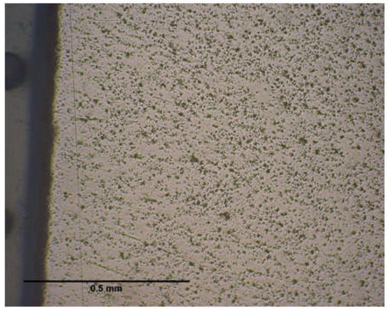


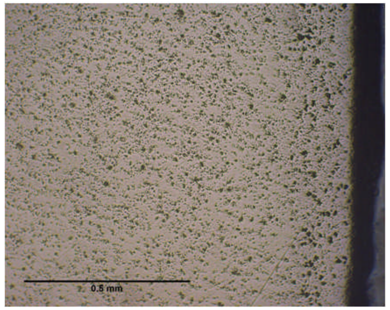
Above the cover





Inside of flux





YSZ tube was stable during SOM electrolysis

Summary (SOM Process for Yb Production)

- Ytterbium oxide was reduced by the SOM Process
- Identified a low melting (700 C) and stable flux system (21 w% LiF and 79 w% YbF_3) for use in the SOM process. The flux dissolved 11 w% Yb_2O_3.
- Confirmed that the yttria-stabilized zirconia (YSZ) tube used as the solid oxide membrane was stable in the flux system for the duration of the experiment.
- Established a process for successfully lowering the valence state of Yb from 3+ to 2+ prior to producing the Yb metal by the SOM electrolytic process.
- Used carbon as the anodic feed and successfully measured the efficiency of the SOM electrolytic process.

Future Work (SOM Process)

- Investigate long-term stability of stabilized zirconia
- Quantify volatility of flux and the resultant change in flux composition
- Quantify process efficiency using real-time chemical analysis
- Explore impurity removal (more electronegative elements) prior to metal deposition
- Perform SOM electrolysis of more multivalent metals (transition metals)
- Investigate use of alternate anodes (oxygen producing inert anodes)
- Perform process modeling and scaleup.

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